
GENERAL REVIEW

Selection of Modifying Additives for Improving the Steam Tolerance of Methane Afterburning Palladium Catalysts

M. A. Mashkovtsev^a, A. K. Khudorozhkov^{b,c}, I. E. Beck^{b,c}, A. V. Porsin^b, I. P. Prosvirin^b,
V. N. Rychkov^a, and V. I. Bukhtiyarov^{b,c}

^aUral Federal University, ul. Mira 19, Yekaterinburg, 620002 Russia

^bBoreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, pr. Akademika Lavrentyeva 5,
Novosibirsk, 630090 Russia

^cNovosibirsk State University, ul. Pirogova 2, Novosibirsk, 630090 Russia

Abstract—In this work, we discuss the problem of the afterburning of methane from the exhaust gases of automobile engines fueled by natural gas. In exhaust neutralizers, the PdO/Al₂O₃ catalyst, the main drawback of which is the reduction of its activity under the action of steam that always present in exhaust gases, is commonly used. To improve the tolerance to steam, a series of PdO–Me_xO_y/Al₂O₃ binary catalysts (Me is Co, Cu, Fe, Ni, Mn, or Sn) was prepared and studied. Comparative tests under conditions modeling the methane afterburning process in automobile neutralizers show that Pd catalysts promoted with nickel, cobalt, and tin oxides are more resistant to the inhibiting action of steam. The high crystallinity of supported PdO and its uniform distribution over the surface of modified Al₂O₃ are indicated as criteria for the stability of catalysts in the presence of steam. Optimization of the concentration of promoters and the preparation method used for their introduction allows the deactivation of Pd catalysts under the action of steam to be almost completely eliminated.

Keywords: bimetallic supported Pd catalysts, deactivation in the presence of water, methane oxidation, X-ray diffraction analysis, X-ray photoelectron spectroscopy, stability.

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INTRODUCTION

The interest in natural gas as a motor fuel is growing all over the world [1–3]. For Russia, with its enormous reserves of natural gas, the transition of at least some motor vehicles to natural gas is especially topical and timely. Natural gas engines are considered to be more environmentally friendly than traditional gasoline and diesel engines, as they produce lower emissions of carbon dioxide and soot. Of special attraction is the possibility of such engines to operate under conditions of great air excess, as this ensures high efficiency and lower temperatures of the burning of fuel, thus reducing emissions of CO and N_xO_y. Nevertheless, incompletely burned methane—the basic natural gas component that is the least reactive and oxidizable one all among the hydrocarbons—remains in exhaust gases. Despite its relatively high chemical inertness, methane is classified as a greenhouse gas [4]; the greenhouse effect of CH₄ is an order of magnitude higher than that of CO₂ at the same level of emission, due to the absence of natural consumers of methane and its long life time in the atmosphere. For this reason, emissions of methane are restricted by law. The catalytic oxidation of CH₄ is the most efficient way to reduce its emissions and to meet the requirements for the concentration of methane in exhaust gases.

Noble metal-based catalysts and metal oxide systems are used for the oxidation of CH₄, but the latter are active only at $T \gg 500^\circ\text{C}$ [5–11]. Only Pd catalysts can ensure high activity in the low-temperature ($<500^\circ\text{C}$) oxidation of methane [1–6, 12], but they are easily deactivated and very sensitive to the presence of steam in the reaction medium. The problem of the deactivation of catalysts in the presence of water (which is a product of the catalytic methane afterburning and is always present in excess in exhaust gases) is the most complicated one. For this reason, the solution of this problem is a necessary condition for using Pd catalysts in the neutralizers of gas-fueled automobile engines [1–3, 13]. The main hypotheses on the mechanism of Pd catalysts deactivation are based on the water-induced conversion of PdO active in the oxidation of methane into low-active surface hydroxide, the stability of which is lowered with an increase in temperature, that's why the inhibiting action of water is manifested most pronouncedly at $T < 450^\circ\text{C}$ [14]. The removal of water from the surface O–H groups with the regeneration of the active phase of PdO is the limiting reaction stage in the low-temperature region, as confirmed by the experimentally determined reaction order with respect to water of nearly –1 [15]. At higher temperatures ($>500^\circ\text{C}$), the C–H bond rupture

in the methane molecule becomes the limiting reaction stage, and the reaction order with respect to water is reduced to zero [16].

One of the methods for increasing the activity of supported Pd catalysts and/or their resistance to deactivation under the action of steam is replacing them with PdO— MeO_x /Al₂O₃ bimetallic systems (where *Me* is Cu, Mn, Cr, Ni, Co, Ce, or Fe) [17–21]. The contradictory information in the literature hampers the choice of a suitable oxide promoter. For example, it is shown in [17] that the introduction of Ni, Co, Ce, or Fe oxides increases the activity of Pd/Al₂O₃ catalysts, whereas Cu, Mn, or Cr oxide additives have a negative effect. In [18, 20], however, it was stated that the modification of Al₂O₃ with Mn oxides (up to 18 wt %) increases the activity of Pd catalysts and improves their resistance to deactivation, and some decrease in the activity of Pd-catalysts upon the introduction Co or Ni is noted in [19]. It seems likely that the influence of the second component on the activity of a Pd catalyst depends on of the temperature range of the reaction [17] and on the method which is used for the preparation of a catalyst and determines its phase composition and dispersion, as well as the degree of the interaction between its components [21]. In most works [17–20], the activity of catalysts was studied without adding steam to initial methane–air mixtures, thus creating a fundamental distinction in the operational conditions of such catalysts. The presence of steam in a gas flow can considerably change the ranking of catalysts. For example, Co additives reduce the activity of a Pd catalyst during the oxidation of CH₄ in dry feed, whereas no lowering of activity is observed in wet feed [21]. A more pronounced effect is observed for Pd—NiO/Al₂O₃ catalysts, the ignition temperature on which is higher (372°C) than that on the Pd/Al₂O₃ catalyst (345°C) in dry feed, but falls (to 372 and 400°C, respectively) upon the addition of 1% of steam, and the difference between the ignition temperatures grows with an increase in the wetness of the feed [22]. In [12], the correctness of the kinetic data obtained in flow reactors using dry feed was questioned, as the strong deactivation of the catalyst by water formed in the reaction leads to a nondifferential regime.

The ability of some oxide promoters to accelerate the desorption of water from the surface of PdO may be considered as a possible cause of the decrease in the inhibiting effect of steam. This hypothesis is partially confirmed by the kinetic studies [22], where the influence of an added oxide on the enthalpy of the desorption of water from the surface of palladium oxide was revealed (in particular, the positive effect of nickel and tin oxides on this process was demonstrated).

Comparative tests of catalysts of the low-temperature oxidation of methane under conditions simulating the operation of catalytic neutralizers in the presence of 10–15% of steam in a gas mixture fed into a cellular block catalyst as the major condition are of

special interest. In this work, we added up to 10% of modifying oxide additives into the CH₄ afterburning Pd catalysts to improve their tolerance to H₂O vapor. A number of cordierite block supported binary PdO— Me_xO_y /Al₂O₃ catalysts (*Me*—Co, Cu, Fe, Ni, Mn, or Sn) were prepared and studied. Tests were performed under lean-burn conditions simulating the real CH₄ afterburning process in the neutralizers of natural gas engines. The influence of a promoter on the activity of Pd catalysts of the complete methane oxidation under the condition of dry and wet feed, and the change in the physicochemical characteristics of supported PdO (including the size of particles, the PdO decomposition temperature, the binding energy of Pd 3*d*-core level, and the surface concentration of palladium in catalyst samples) were studied.

EXPERIMENTAL

Preparation of Catalysts

Powdered Al₂O₃ (SASOL, Puralox SCFa-200/Zr3; specific surface, 200 m²/g) modified with 3% of ZrO, was used as a support for our Pd catalysts. The active component was deposited onto supports premodified with an oxide promoter. The concentration of promoting oxides and palladium in all the samples was nearly 10 and 2 wt %, respectively. A list of the prepared catalysts, together with their composition and characteristics, is given in the table.

NiO, Co₃O₄, α-Fe₂O₃, and MnO₂ (samples II, III, V, and IX, respectively) were introduced into Al₂O₃ via its wet impregnation with corresponding metal nitrates for 1 h, and the excess solvent was withdrawn on a rotary evaporator in water-jet pump vacuum. SnO₂ (sample IV) was introduced via the incipient wetness impregnation of the support with a Sn(II) acetate solution in glacial acetic acid. After impregnation, the modified supports were dried at 120°C and then calcined for 2 h at 300 (samples II and III), 400 (V and IX), or 600°C (IV). Magnetite Fe₃O₄ was precipitated with aqueous ammonia from a stoichiometric mixture of Fe²⁺ and Fe³⁺ salts. The resulting suspension was then deposited onto aluminum oxide, the mother liquor was decanted, and the sample was dried at 120°C and calcined at 300°C (sample VI).

The Mn₃O₄ phase (sample X) was obtained by surface self-propagating thermosynthesis [8], i.e., via the impregnation of alumina with a solution of Mn²⁺ nitrate and Mn³⁺ acetylacetonate mixed in a molar ratio of 1 : 1 with the subsequent initiation of flameless burning in the course of drying at 120°C. When depositing CuO (sample VII), we also applied thermosynthesis to reduce the size of oxide promoter particles and used an equimolar mixture of Cu(NO₃)₂ and Cu(CH₃COO)₂ as precursors. Samples VII and X were then calcined for 2 h at 400°C. When preparing sample VIII, we first formed the Cu₂O phase on the sup-

Phase composition and physicochemical characteristics of fresh Pd-catalyst samples

Sample	Promoter concentration (in terms of an oxide), wt %	XRD		XPS			DTA-DTG		
		Promoter phase Me_xO_y	Crystallite size, nm		Binding energy of electrons, eV			[Pd]/[Al] atomic ratio* ⁶	Promoter charge state
			Me_xO_y promoter	PdO	Pd3d _{5/2}	promoter (level)			
I	—	—	—	3.7	336.2	—	0.003	880.0	
II	10.5	NiO* ¹	3.7	3.4	336.5	856.2 (Ni2p)	0.004	886.9	
III	9.6	Co ₃ O ₄ * ²	11.2	4.0	336.6	780.4 (Co2p)	0.001	892.7	
IV	9.1	SnO ₂	6.5	2.8	336.6	486.6 (Sn3d)	0.012	893.3	
V	10.3	α -Fe ₂ O ₃ * ³	8.1	3.8	336.6	710.6 (Fe2p)	0.032	902.3	
VI	9.9	γ -Fe ₂ O ₃ * ³	7.1	4.6	336.3	710.3 (Fe2p)	0.021	898.1	
VII	8.9	CuO* ⁴	9.4	3.9	337.0	933.5 (Cu2p)	0.017	960.0	
VIII	9.4	Cu ₄ O ₃ * ⁴	4.2	4.2	337.2	933.1 (Cu2p)	0.002	931.1	
IX	9.6	MnO ₂ (major)* ⁵ + Mn ₂ O ₃	13.1	3.8	336.2	642.0 (Mn2p)	0.095	888.2	
X	9.8	Mn ₃ O ₄ * ⁵	4.3	4.0	337.7	641.0 (Mn2p)	0.011	927.7	

Note: *¹ The predominance of Ni²⁺ in the sample is additionally indicated by the presence of an intense satellite with a binding energy of 862.2 eV in its X-ray photoelectron spectrum.

*² In the X-ray photoelectron spectrum, the presence of a satellite shifted by 7.5 eV towards higher binding energies from the basic line serves as an additional indication of the predominance of Co₃O₄ in the sample, instead of cobalt spinel CoAl₂O₄.

*³ The presence of a satellite, which is shifted by 8.5 eV toward higher binding energies from the basic Fe2p line and absent in the X-ray photoelectron spectrum of Fe₃O₄, serves as an additional indication of the predominance of Fe₂O₃ in the samples.

*⁴ The predominance of Cu²⁺ in sample VII is additionally indicated by the presence of an intense satellite, which has with a binding energy of 942 eV and is absent in the X-ray photoelectron spectrum of the Cu¹⁺ compounds; this satellite in the spectrum of sample VIII has a much lower intensity at comparable values of the amplitudes of the Cu2p level's basic signal.

*⁵ DTA curve endothermic peaks, which are accompanied by the loss of mass and correspond to the phase transitions MnO₂ → Mn₂O₃ (~600 °C) and Mn₂O₃ → Mn₃O₄ (~960 °C) not detected in the DTA curves of sample X, are additional indications of the predominance of MnO₂ in sample IX.

*⁶ According to the intensity ratio of the Pd3d and Al2p lines in an X-ray photoelectron spectrum and in consideration of the corresponding sensitivity factors.

port surface. To accomplish this, we dried the support impregnated with copper nitrate at 200°C to obtain supported basic copper nitrate $\text{Cu}_2(\text{NO}_3)(\text{OH})_3$, which was reduced with a stoichiometric mixture of hydrazine hydrate in an aqueous suspension with the subsequent wet impregnation with palladium nitrate without intermediate drying.

Palladium was deposited onto alumina (reference sample I) or onto support samples modified with oxide promoters (II–X) via their wet impregnation with an aqueous solution of palladium nitrate. The resulting suspensions were dispersed in a ball mill and then deposited in measured amounts onto cellular cordierite honeycomb cores, which were further dried at 120°C and then calcined for 2 h in a hot air flow at 550°C. The geometric characteristics of each core were a cell density of 62 per cm^2 , a wall thickness of 0.174 mm, a length of 76 mm, and a diameter of 25 mm. The total weight of the powdered catalyst deposited onto a core was nearly 3.1 g. The resulting concentration of Pd in the block catalyst was 0.004 wt % or 1.4 g/l.

Catalyst Characterization Methods

The elemental analysis of the catalysts was performed by atomic emission spectroscopy with inductively coupled plasma on an Optima 4300DV instrument.

The X-ray diffraction analysis of calcined samples was carried out on a Ultima IV universal powder X-ray diffractometer with a copper cathode using CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$). Phases were identified with the use of the demo X-ray Inorganic Crystal Structure Database (ICSD). The sizes of crystallites were determined from the broadening of diffraction peaks via Sherrer's method.

The decomposition temperature of palladium precursor and PdO as well as the temperature of the phase transformations of oxide promoters in samples were determined by differential thermal analysis (DTA) in combination with thermogravimetric analysis (TGA) on a Mettler TGA/SDTA851 instrument. The analysis was conducted by heating a sample from room temperature to 1000°C at a rate of 10°C/min in air; $\alpha\text{-Al}_2\text{O}_3$ was used as the reference sample.

The surface concentration of palladium and a promoter as well as their charge state were determined by X-ray photoelectron spectroscopy (XPS). X-ray photoelectron spectra were recorded on a SPECS photoelectron spectrometer with a Phoibos-150 MCD-9 hemispherical analyzer (AlK_α radiation, $h\nu = 1486.6 \text{ eV}$). The scale of binding energies was precalibrated using $\text{Au } 4f_{7/2}$ and $\text{Cu } 2p_{3/2}$ core level peaks (84.0 and 932.7 eV, respectively).

Catalytic activity tests were performed on a Analytical Emissions System with the use of a gas mixture of the following composition (wt %): O_2 , 4.00; CH_4 ,

0.10; CO , 0.05; NO_x , 0.10; CO_2 , 10.0; H_2O , 12.0; res. N_2 (wet feed). The gas hourly space velocity was nearly 70000 h^{-1} . The wet feed simulated the composition of exhaust gases of lean-burn automobile engines fuelled by natural gas. To reveal the inhibiting action of water vapor, we performed comparative tests in the absence of steam in the initial gas mixture (dry feed). An initial gas mixture was heated at a rate of 10°C/min by IR radiation before being fed into a reactor equipped with a block catalyst sample. For the comparative analysis of ignition curves, we used the average temperature between the inlet and outlet temperatures of the gas mixture. The activity of catalysts was estimated from the temperature of 50% methane conversion (T_{50}).

RESULTS AND DISCUSSION

The phase and chemical compositions of the calcined catalyst samples are given in the table. The main problems in the preparation of catalysts are the synthesis of modified support samples with monophasic middle-dispersion particles of an oxide promoter and the ensuring its direct contact with the active component.

For most samples, the diffraction peaks of tetragonal palladium oxide (palladinite) and the individual oxide promoter phase represented by bunsenite NiO (sample II), cobalt spinel Co_3O_4 (III), cassiterite SnO_2 (IV), hematite $\alpha\text{-Fe}_2\text{O}_3$ (V), maghemite $\gamma\text{-Fe}_2\text{O}_3$ (VI), tenorite CuO (VII), and hausmannite Mn_3O_4 (X) can easily be distinguished in the X-ray diffraction patterns (Fig. 1). Only in sample IX does the major oxide promoter phase (pyrolusite MnO_2) contain a minor impurity phase (bixbyite Mn_2O_3 , < 15 %). The set of diffraction peaks, which do not correspond to any of the individual palladium or copper oxides described above and are located between the lines of palladinite PdO and paramelaconite Cu_4O_3 , allows us to assume the formation of a mixed oxide Pd–Cu phase with a tetragonal lattice in sample VIII.

The average sizes of the coherent scattering regions of the active component and oxide promoter crystallites in the catalysts were calculated using Sherrer's method (see table). It can be seen that the modifying component in most samples is well crystallized and represented by individual phase particles with an average size of 6–9 nm, the largest size of oxide promoter crystallites (13 nm) is typical of sample IX, while the smallest size of oxide promoter crystallites (nearly 4 nm) is characteristic of samples II, VIII and X. The size of the crystallites of palladium oxide (the active component) is approximately the same for all of the samples (3–5 nm), and we thus might expect that the PdO surfaces accessible for reaction are comparable, i.e., the different catalytic activities are not due to changes in dispersion.

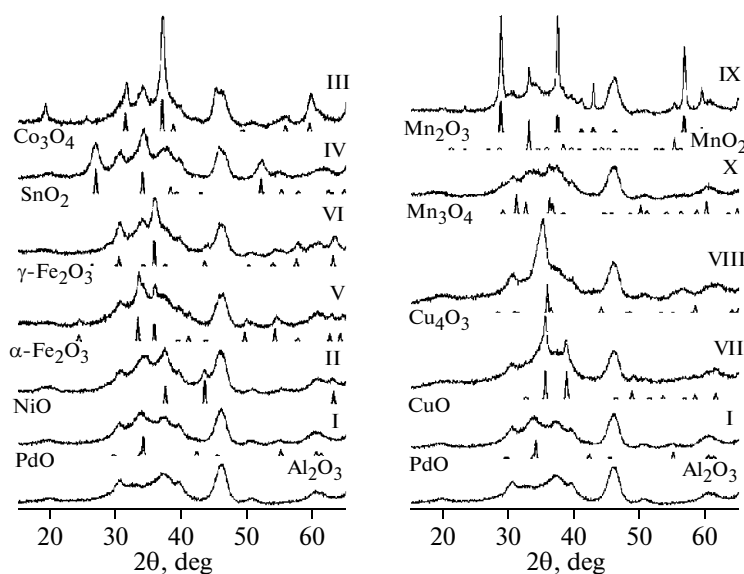


Fig. 1. X-ray diffraction patterns of monometallic I and bimetallic II–X catalyst samples. The X-ray diffraction pattern of the pure Al_2O_3 support is given for comparison. The location of the main reflections of the pure phase of an oxide promoter or palladium oxide is shown below each experimental X-ray diffraction pattern according to the ICSD data.

One of the criteria for estimating the interaction of the active component PdO with an oxide promoter may be the change in the temperature of the $\text{PdO} \rightarrow \text{Pd}$ phase transition in bimetallic samples II–X, in comparison with that for monometallic sample I. The PdO formation process, which proceeds in two stages at $\sim 250^\circ\text{C}$ ($-\text{H}_2\text{O}$) and $\sim 350^\circ\text{C}$ ($-\text{2NO}_2$, $-\text{O}_2$) during the thermal decomposition of dried catalyst samples in air, was preliminary studied. The decomposition of newly synthesized PdO within the broad temperature range from 800 to 950°C indicates the formation of different forms of the active component. PdO is

formed in a single stage simultaneously with the phase of a promoting oxide upon the deposition of palladium precursor onto an underformed oxide promoter. According to the TGA data (see table), the thermal decomposition of PdO in precalcined catalyst samples proceeds within a narrower temperature region with a sharply pronounced decomposition temperature T_d of $880\text{--}960^\circ\text{C}$, depending on the composition of the sample. These temperatures are much higher than the existing operational temperature range of any neutralizer, so we shall consider T_d only as a value characterizing the degree of interaction between PdO and an oxide promoter.

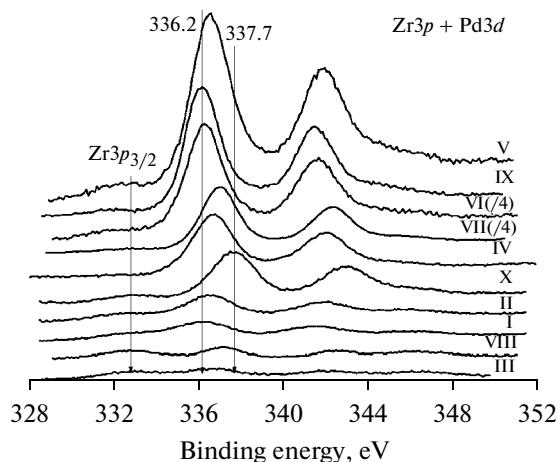


Fig. 2. X-ray photoelectron spectra of the Pd3d region of the investigated monometallic I and bimetallic II–X Pd-catalyst samples. The spectra were normalized to the intensity of the $\text{Al}2p$ signal in the samples.

The lowest PdO decomposition temperature is observed for monometallic sample I. In all the cases, some increase in the decomposition temperature of PdO (a minimum of $7\text{--}8^\circ\text{C}$ for samples II and IX promoted with NiO or MnO_2 and a maximum of $48\text{--}80^\circ\text{C}$ for samples VII, VIII and X promoted with copper oxides or Mn_3O_4) is observed upon the addition of oxide promoters.

According to the XPS data, the effect of an oxide promoter is also revealed as a change in the binding energy of PdO electrons, relative to that of monometallic sample I. In all studied samples, the binding energy of Pd 3d-level is close to the individual PdO binding energy, 336.7 eV , thereby indicating the Pd^{2+} charge state (see the table and Fig. 2). The binding energy of Pd 3d-level in sample I is slightly lower (336.2 eV) than that for bulk PdO, probably due to the interaction with Al_2O_3 .

The shift in the binding energy of Pd 3d-electrons towards higher values upon the introduction of an

oxide promoter relative to the binding energy in sample I agrees with the increase in the decomposition temperature of PdO. The greatest increase in binding energy (337.7 eV) is observed for sample X promoted with Mn_3O_4 , and the Pd 3d-level binding energy grows considerably for samples VII and VIII promoted with copper oxides.

A comparative analysis of the X-ray photoelectron spectra of samples I–X (see the table and Fig. 2) shows considerable distinctions in the enrichment of the surface of alumina support particles with palladium oxide (an increase in the surface $[\text{Pd}]/[\text{Al}]$ atomic ratio), depending on the nature of the oxide promoter at the same percentage of palladium in the catalysts. Taking this into account, the studied catalysts can be classified into two groups: samples II, III, and VIII, whose surface $[\text{Pd}]/[\text{Al}]$ atomic ratios differ slightly from that of reference sample I, and all the others, for which this ratio grows many times (including several tens of times as, e.g., for samples V and IX).

The dependences of the methane conversion on the average temperature of a catalytic block (ignition curves) under the condition of dry or wet feed are shown in Fig. 3. The addition of oxide promoters into a catalyst under the condition of dry feed is more likely to have a negative effect on the low-temperature activity of Pd catalysts in the oxidation of CH_4 . The deactivation of samples II, III, IV, and IX promoted with NiO , Co_3O_4 , SnO_2 , and MnO_2 is weakly pronounced (a 3–8°C increase in ΔT_{50}), whereas the addition of iron oxides (samples V and VI), Mn_3O_4 (sample X), and copper oxides (samples VII and VIII) raises T_{50} by 20–30, 57, and 70–100°C, respectively.

The presence of steam in the initial gas mixture considerably lowers the activity of all the Pd catalyst samples (see Fig. 3b), e.g. $\Delta T_{50} = 76^\circ\text{C}$ for monometallic sample I. Such a decrease in the activity is typical for the oxidation of methane on $\text{PdO}/\text{Al}_2\text{O}_3$ catalysts upon the addition of steam, and agrees with the data [1–3].

However, the positive effect of some oxide promoters becomes very clear under these near-real operational conditions of automobile neutralizers. The activity of catalysts III and IV promoted with cobalt and tin oxides is already appreciably higher than the activity of nonpromoted sample I (T_{50} is 15°C lower), a fortiori nickel oxide modified sample II, on which the ignition temperature is lowered by 45°C. If the increase in the ignition temperature (ΔT_{50}) upon the addition of H_2O vapor for the same catalyst sample is considered as a steam tolerance criterion, we may speak about the positive effect not only of nickel, tin, and cobalt oxides (ΔT_{50} is 24, 52, and 58°C, respectively), but of MnO_2 and $\alpha\text{-Fe}_2\text{O}_3$ (ΔT_{50} is 69 and 71°C, respectively) as well.

In this work, we revealed several criteria for the qualitative estimation of the existence of direct contact

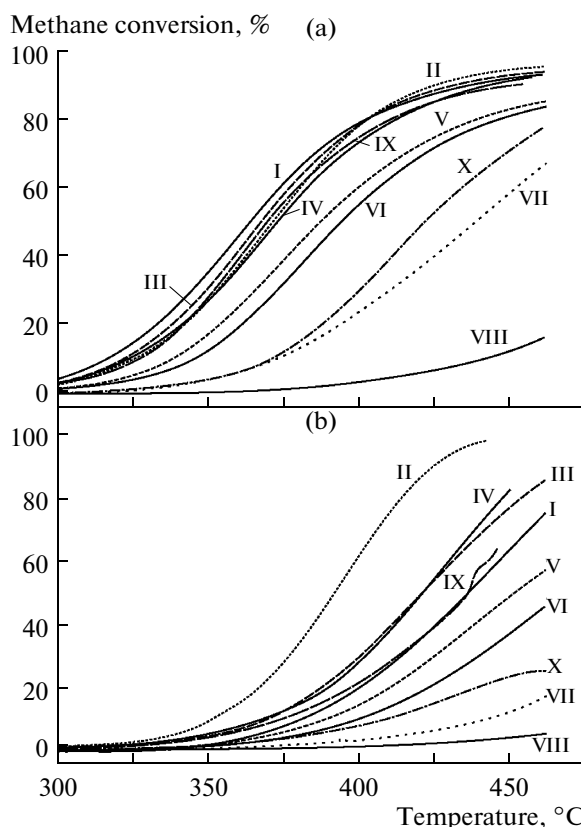


Fig. 3. Methane ignition curves on samples I–X in the (a) absence and (b) presence of 12 vol % of steam in the initial gas mixture.

between components in a binary catalyst via their mutual influence:

- (1) the change in the decomposition temperature of supported PdO, relative to that in monometallic sample I (the increase in T_d is more or less typical for all the bimetallic catalysts, especially for samples VII, VIII, and X);
- (2) the change in the temperature of the phase transitions of an oxide promoter (observed for sample IX and equal to 40°C);
- (3) the change in the binding energy of Pd 3d-level;
- (4) the change in the surface concentration of Pd (a 30-fold enrichment of the surface with palladium in sample IX and a 6- to 10-fold enrichment in samples VII, VI, and V);
- (5) the shift of peaks in the X-ray diffraction patterns of bimetallic samples, relative to monometallic analogues (strongly pronounced for sample VIII, thus indicating the formation of a new mixed oxide phase, and observed to a lower degree for a number of other samples, due to changes in the parameters of their crystal lattice);
- (6) the change in the width of diffraction peaks, due to the change in the sizes of supported PdO or oxide promoter particles in binary samples;

(7) the stabilization of the charge state (e.g., Cu^+ in sample VIII) or the phase of an oxide promoter (maghemite in sample VI) in the presence of Pd in comparison with Pd-free samples.

Since at least one of the characteristics summarized in the table satisfy some of the mentioned criteria for each sample, we may conclude that direct contact between the components of a catalyst is attained for each sample. However, the promoters affect the properties of supported palladium oxide to different extent, and this seems to be reflected in changes in the catalytic activity of samples during the oxidation of methane and in their sensitivity to poisoning with water. It is obvious that the formation of the new mixed phase in sample VIII has an extremely negative effect on the activity of Pd in the oxidation of CH_4 , as manifested in the testing of this sample both under the conditions of dry and wet feed. The high PdO decomposition temperature and increased Pd $3d$ -level binding energy, which are typical of this sample and testify to the very strong influence of the second component, are not unique. Similar effects appear upon doping Pd catalysts with CuO (sample VII) or Mn_3O_4 (sample X), which are also characterized by very low activity in both testing regimes. In the least active catalyst samples (VIII, VII, X, and VI), a modifying additive presented as an oxidizable (Cu_2O , Fe_3O_4) or highly-defective thermosynthesized (CuO , Mn_3O_4) phase before the deposition of Pd, and this could predetermine the strong interaction between the forming PdO and the oxide promoter phases. The much lower activity of Pd–Sn catalysts prepared by the deposition of Pd onto Al_2O_3 modified with Sn(II), and of thermosynthesized Pd–Co or Pd–Fe catalysts (data were not given), could serve as an additional argument for this hypothesis.

Both samples (V and VI) promoted with iron oxides exhibit low-temperature activity in the oxidation of methane, but it is still appreciably lower than the activity of monometallic sample I. Since the principal distinction of these samples is the enrichment of their surface with palladium, we may presume that this factor also has a negative effect on the catalytic activity, due probably to an increase in the fraction of palladium accessible for poisoning with water. This hypothesis is supported by catalysts V–VII and IX, which have higher surface Pd concentrations (see table) relative to those of the most active samples I, II, and III, which exhibit the lowest activity among the studied samples in the oxidation of methane in the presence of water (see Fig. 3b).

In analyzing the characteristics of supported palladium oxide in NiO, Co_3O_4 , and SnO_2 promoted catalyst samples II–IV most resistant to the inhibiting effect of water, our attention was drawn to the narrow Pd $3d$ -electron binding energy range observed for these samples: $E_{\text{bind}} = 336.5\text{--}336.6$ eV is very close to E_{bind} of individual PdO (336.7 eV). Note that the bin-

ding energy of reference sample I and MnO_2 modified sample IX (similar to the former in its activity) is slightly lower (336.2 eV).

It follows from the above that the highest activity under near-real conditions and the highest steam tolerance of nickel oxide promoted catalyst II results from the simultaneous ensuring of the following conditions: the optimum charge state of palladium (E_{bind} of Pd $3d$ -level is 336.5 ± 0.1 eV), high structure ordering of supported PdO (concluded from the manifestation of even low-intensity diffraction peaks and a slight decrease in the lattice parameter) though a comparatively small size of its particles under the uniform distribution of the active component and a promoter over the volume of alumina based support particles. Samples III and IV promoted with cobalt and tin oxides satisfy all these criteria to a slightly lower degree as compared with the monometallic analogue I, excluding some distortion in the uniformity of the distribution of palladium between the surface and the volume of Al_2O_3 particles towards the enrichment or depletion of their surface (samples IV and III, respectively). Enrichment of the surface with palladium has a much more negative effect on the activity of catalysts V and IX, which are promoted by iron and manganese oxides and, according to the two remaining criteria, would demonstrate quite higher activity and tolerance to the action of steam.

These conclusions are preliminary, as the changes of the samples under the reaction conditions were not taken into consideration. Many of the processes associated with changes in the state of Pd (and in turn affecting catalytic activity) can proceed even in a monometallic catalyst. Among these are the changes in the charge state of palladium and in the size and morphology of active component particles under rather severe reaction conditions and the action of reagents or reaction products, the interaction with Al_2O_3 support, the migration of the active component along the active layer depth, etc. In bimetallic catalysts, this scenario becomes more complicated, as the change in the size and morphology of oxide promoter particles, the formation of spinels (e.g., CoAl_2O_4 or NiAl_2O_4 [17, 19]), the strengthening or weakening of the interaction between the active component and a promoter right up to the formation of new mixed phases or to the complete separation of surface phases, the diffusion of one or another component deep into the layer or its exposure on the surface, etc., also become possible. A final conclusion regarding the nature of the influence of an oxide promoter in bimetallic samples (positive or negative) can be made only by revision analysis of the samples after their aging under reaction conditions.

CONCLUSIONS

We prepared and tested nine samples of cellular cordierite block supported catalysts promoted with Ni, Co, Sn, Fe, Mn, or Cu oxides to study the influence of promoters on the tolerance of low-temperature methane oxidation Pd catalysts to the inhibiting action of water, which is a product of the oxidation of methane on the catalyst and is always present in excess in exhaust gases. The results show that the stability of Pd catalysts at a considerable concentration of steam in the feed can be improved by introducing certain oxide promoters. Cobalt and tin oxides can serve as such promoters, although the greatest effect is attained in the case of NiO. The high crystallinity of supported PdO and its uniform distribution over the surface of modified Al₂O₃ at weak PdO–support interaction provided by the deposition of the palladium precursor onto a completely formed oxide promoter phase stable within the range of existing reactor temperatures (<550°C) were selected as criteria for the preservation of catalytic activity in the presence of steam. The deactivation of a Pd catalyst under the action of steam can be completely eliminated by optimizing the concentration of NiO, Co₃O₄, or SnO₂ and the support modifying method.

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